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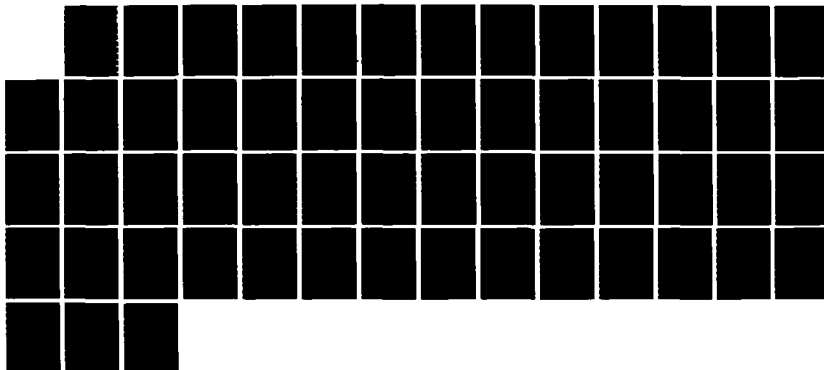
QUANTUM CHEMICAL INVESTIGATIONS OF THE MECHANISM OF
CATIONIC POLYMERIZATION (U) JOHNS HOPKINS UNIV BALTIMORE
RD J J KAUFMAN 15 NOV 85 TR-6 N00014-80-C-0003

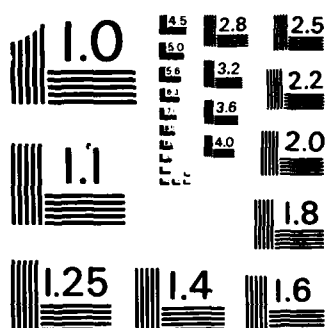
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I. In anticipation of significant access to the NRL CRAY XMP-12 supercomputer we devoted major attention this past year to converting our programs to that computer, which runs under a COS operating system. We converted the following programs to the NRL CRAY XMP-12: MOLASYS, MRD-CI, CASSCF, INTER-MOLASYS, CRYSTAL and POLY-CRYST. We also meshed in with the MRD-CI program our own ab-initio MOLASYS MODPOT/VRDDO/MERGE program which contains a number of desirable computational strategies for ab-initio calculations on large molecules as well as procedures for strictly orthogonal localization of molecular orbitals.

II. As a preliminary to carrying out MRD-CI calculations on the attack of oxetane on protonated oxetane in the propagation step of cationic polymerization, we initiated MRD-CI calculations on opening the oxetane ring and the protonated oxetane ring. These calculations were carried out using

strictly orthogonal localized orbitals in the region of the $O-C \begin{smallmatrix} H \\ (4) \\ H \end{smallmatrix}$ bond being opened with the remainder of the occupied molecular orbitals being folded into an effective CI Hamiltonian. We monitored the dominant configurations in the final wave functions as a function of the R_{O-C} bond distance. We also continued our ab-initio MODPOT and electrostatic molecular potential contour calculations around substituted oxetanes. Among those we calculated were BNMAMO and MNMAMO.

III. We carried out MRD-CI calculations for the dissociation of the $>C-NO_2$ bond in nitrobenzene. Since it is not unambiguous how best to localize molecular orbitals in an aromatic system we carried out the calculations based on local canonical orbitals in the region of the $>C-NO_2$ portion of the nitrobenzene. MRD-CI calculations were carried out for the lowest roots of all eight electronic states: 1A_1 , 3A_1 , 1A_2 , 3A_2 , 1B_1 , 3B_1 , 1B_2 and 3B_2 as a function of $C-NO_2$ distance. By monitoring the dominant configurations of the various molecular orbital fillings as a function of $>C-NO_2$ distance it is possible to determine accurately how many times a particular potential energy surface changes dominant configuration. A number of the higher electronic states were predissociative. These predissociative states have significant implications for the initiation of detonation.

IV. We continued testing of our POLY-CRYST program for ab-initio calculations in crystals and polymers.

V. We also implemented further additions to the INTER-MOLASYS program including the capability of calculating the dispersion energy contributions by a variation-perturbation procedure. We have also calculated further ab-initio atom class-atom class potential functions. *Keywords:*

Report Number ONR-NR093964-TR6

SUMMARY

ANNUAL REPORT

QUANTUM CHEMICAL INVESTIGATIONS OF THE MECHANISM OF CATIONIC
POLYMERIZATION

and

THEORETICAL PREDICTION OF CRYSTAL DENSITIES

and

DECOMPOSITION PATHWAYS OF ENERGETIC MOLECULES



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Dr. Richard Miller, ONR Contract Monitor
Dr. David R. Squire, ARO Contract Monitor

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CONCISE SUMMARY

In anticipation of significant access to the NRL CRAY XMP-12 supercomputer we devoted major attention this past year to converting our programs to that computer, which runs under a COS operating system. We converted the following programs to the NRL CRAY XMP-12: MOLASYS [Gaussian integrals (including special options for large molecules), SCF, Properties]; MRD-CI (Gaussian Integrals, Adapt, SCF, Transformations, Multireference double excitation, CI); CASSCF (Gaussian integrals, SCF, Properties, Transformation, MCSCF); INTER-MOLASYS (Integrals, SCF, Intermolecular SCF, Special routines for ab-initio energy partitioned contributions for ab-initio atom class-atom class potentials as input for CRYSTAL); CRYSTAL (optimization of crystal unit cell parameters); POLY-CRYST [Crystal and Polymer SCF and integrals (for repeating units)]. We also meshed in with the MRD-CI program our own ab-initio MOLASYS MODPOT/VRDDO/MERGE program which contains a number of desirable computational strategies for ab-initio calculations on large molecules as well as procedures for strictly orthogonal localization of molecular orbitals.

As a preliminary to carrying out MRD-CI calculations on the attack of oxetane on protonated oxetane in the propagation step of cationic polymerization, we initiated MRD-CI calculations on opening the oxetane ring and the protonated oxetane ring. These calculations were carried out using strictly orthogonal localized orbitals in the region of the $O-C \begin{smallmatrix} H \\ \diagup \\ (4) \end{smallmatrix} -H$ bond being opened with the remainder of the occupied molecular orbitals being folded into an effective CI Hamiltonian. We carried out calculations with

our ab-initio MODPOT basis set and with an all-electron basis set contracted to 3^S2^P . We monitored the dominant configurations in the final wave functions as a function of the R_{O-C} bond distance. We are now initiating MRD-CI calculations on the attack of oxetane on protonated oxetane, with a formation of an $O-C$ bond between the two rings and opening of the $O-C_{(4)}$ bond in the protonated oxetane ring. These calculations are being carried out based on strictly orthogonal localized orbitals in the region extending over the new bond being formed and the opening of the $C-O_{(4)}$ bond. We also continued our ab-initio MODPOT and electrostatic molecular potential contour calculations around substituted oxetanes. Among those we calculated were BNMAMO and MNMAMO.

We carried out MRD-CI calculations for the dissociation of the $>C-NO_2$ bond in nitrobenzene. Since it is not unambiguous how best to localize molecular orbitals in an aromatic system we carried out the calculations based on local canonical orbitals in the region of the $>C-NO_2$ portion of the nitrobenzene. MRD-CI calculations were carried out for the lowest roots of all eight electronic states: 1A_1 , 3A_1 , 1A_2 , 3A_2 , 1B_1 , 3B_1 , 1B_2 and 3B_2 as a function of $>C-NO_2$ distance. By monitoring the dominant configurations of the various molecular orbital fillings as a function of $>C-NO_2$ distance it is possible to determine accurately how many times a particular potential energy surface changes dominant configuration. The ground 1A_1 state is not predissociative. However, the relative contributions of the various determinants change. The 3A_1 state is predissociative. Both the 1A_2 and 3A_2 states are predissociative and both change dominant configuration at least twice along their potential energy surfaces. The 1B_1 state is predissociative and changes dominant configuration at least once along its potential energy surface. The 3B_1 state is very slightly predissociative, changing dominant configuration at least once along its potential energy surface. The 1B_2 and 3B_2 surfaces are predissociative, each changing dominant configuration at least twice along their potential energy surfaces. These results emphasize the necessity of carrying out such MRD-CI calculations for the understanding of dissociation of nitroexplosives and initiation of detonation.

We continued testing of our POLY-CRYST program for ab-initio calculations in crystals and polymers.

We also implemented further additions to the INTER-MOLASYS program including the capability of calculating the dispersion energy contributions by a variation-perturbation procedure. Our testing indicated that this latter contribution is better represented using the virtual orbitals of the two interacting molecules than by just using the virtual orbitals of a single molecule. We have also calculated further ab-initio atom class-atom class potential functions.

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Joyce J. Kaufman, Principal Investigator

I. Conversion of Our Programs to CRAY Vector Supercomputers

In anticipation of significant access to the NRL CRAY XMP-12 supercomputer we devoted major attention this past year to converting our programs to that computer, which runs under a COS operating system. The other CRAY computers on which we ran up until this year have all had various CTSS operating systems. Our programs are large and complicated and also make use of the special mathematics libraries on the computers. None of the CRAY computers we use are completely compatible and thus we have to adapt the programs separately for each computer.

We began converting to the NRL CRAY XMP-12 in March 1985 just as soon as that computer was available. We have had helpful cooperation from the NRL computer center and also interacted closely with them in testing external data transmission.

We had expected that the NRL CRAY XMP-12 would be our major production computer. Thus all of our programs would be under one operating system (COS) which is vital, since many of these large programs have to interface with our other large programs. For some of the programs, assembly language routines have been implemented to make the handling of large data files (integrals, transformed integrals, etc.) much more tractable. These assembly language portions were written in CAL, the CRAY assembly language running under COS. CAL is not available on the CRAY's which run under CTSS.

We converted the following programs to the NRL CRAY XMP-12

- MOLASYS - Gaussian integrals (including special options for large molecules)
 - SCF
 - Properties
- MRD-CI - Gaussian Integrals
 - Adapt
 - SCF
 - Transformations
 - Multireference double excitation - CI

Earlier in this past year before the NRL CRAY XMP became available we had converted the complete MRD-CI program to a CRAY 1M (running under CTSS). This had involved a great deal of rewriting. Then when the NRL CRAY XMP became available we made the MRD-CI program operational on the NRL CRAY XMP.

The NRL machine has sufficient available disc space to make feasible reasonably large MRD-CI calculations on good size molecules. We have been making extensive use of the MRD-CI program both for decomposition of energetic molecules and most recently for the propagation step for cationic polymerization. We also meshed in with the MRD-CI program our own ab-initio MOLASYS MODPOT/VRDDO/MERGE program which contains a number of desirable computational strategies for ab-initio calculations on large molecules as well as procedures for strictly orthogonal localization of molecular orbitals.

- CASSCF - Gaussian integrals
- SCF
- Properties
- Transformation
- MCSCF

We have also vectorized the computer-time-consuming steps of this latter series of programs. All of the I/O routines had to be rewritten to run under COS.

- INTER-MOLASYS - Integrals
- SCF
- Intermolecular SCF
- Special routines for ab-initio energy partitioned contributions for atom class-atom class potentials as input for CRYSTAL

- CRYSTAL - Optimization of crystal unit cell parameters

- POLY-CRYST - Crystals and polymer SCF and integrals (for repeating units)

Our ONR technical contract monitor, Dr. Richard Miller, had even hoped that it would be possible to arrange high speed 55 kilobit data transmission to and from the NRL CRAY to our lab at the Johns Hopkins University. Thus we researched intensively the network and equipment facilities necessary for such transmission. We presented to our ONR technical contract monitor in July 1985 the complete system hardware and software requirements, procedures and persons to contact in DOD Telecommunications. However, in view of the fact that our ONR technical contract monitor and we learned only at that same time of our very limited computer time allotment on the NRL CRAY XMP-12, the high speed data transmission project is on hold for the time being.

However, in mid July 1985 unexpectedly we were informed that only a few hours of computer time would be allotted to us on the NRL CRAY XMP-12. Moreover, the NRL CRAY computer time which was to have been available at no-cost up until October 1, 1985 began being charged (partial rates) as of August 1, 1985.

We have been very fortunate to get computer time on other CRAY computers:

- CRAY 1M - CTSS
- CRAY 1S - COS [but without the special NAG (Nottingham Algorithm Group) library]

Thus, we have also converted some of our programs to these CRAY computers. Our programs are large and complicated and require considerable effort each time we move to a different CRAY since no two of the machines are completely compatible systemwise.

This year we have been carrying out production runs on various CRAY's with a number of our programs.

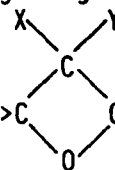
II. Calculations for Cationic Polymerization of Energetic Monomers

The Navy has an interest in energetic polymers made by cationic polymerization from cyclic ethers substituted with exotic energetic pendant groups.

Previous experimental results of Aoki et al. on cationic polymerization of cyclic ethers had indicated that the ease of polymerization was related to the basicity of the cyclic ether and to its ring strain. By generation of electrostatic molecular potential contour (EMPC) maps from ab-initio MODPOT/VRDDO/MERGE quantum chemical calculations we were able to predict correctly the order of the basicity of oxetanes substituted with exotic energetic groups even prior to their actual synthesis. Our EMPC maps also predicted correctly the order of the polymerizability of these substituted oxetanes even prior to the polymerization experiments. Also valuable was our prediction from the EMPC maps that 3,3-dinitrooxetane should not polymerize under ordinary conditions. Experimentally this was shown to be so. Thus, we now even have a "fingerprint" EMPC map which can be compared to EMPC maps calculated even for as yet unsynthesized substituted oxetanes to predict whether or not that particular oxetane will polymerize.

Our calculations of the ring strain for variously substituted oxetanes showed little variation of ring strain with different substituents. Thus the change in the basicity of the oxetanes with substitution was the overriding factor in determining their polymerizabilities.

The propagation step had been suggested earlier by experimentalists to be influenced by the electrophilicity of the resulting ring-opened



"protonated carbocation". For a substituted oxetane $>\text{C}-\text{O}-\text{C}<$, the ring-



opened "protonated carbocation" would be $\text{HO}-\text{CH}_2-\text{C}-\text{CH}_2^+$. There are several

calculated quantum chemical indices which relate to electrophilicity: the charge on the carbon atom of the terminal $-\text{CH}_2^+$, the EMPC map around that

terminal $-\text{CH}_2^+$ and the energies of the unoccupied molecular orbitals of the

"protonated carbocation." We had calculated all of these indices. There was little difference in the charges on the carbon atoms on the terminal

$-\text{CH}_2^+$ group or in the EMPC maps around that group as a function of

substitution. However, there was a significant difference in the energies of the unoccupied molecular orbitals as a function of substitution. On this latter criterion the ring-opened "protonated carbocation" of 3,3-dinitrooxetane was the most electrophilic species. However, 3,3-dinitrooxetane will not polymerize under ordinary conditions because its basicity is too low. Therefore, it is the initiation step rather than the propagation step which is overriding in determining the polymerizability of a monomer.

The next aspect of the mechanism of cationic polymerization is the relative polymerization ratio in copolymerization.

We have been exploring what quantities to calculate to predict relative polymerization ratios. This turns out to be considerably more complicated than initiation. We can predict correctly in a mixture which monomer will initiate first and more quickly. However, propagation is dependent on a number of different and sometimes conflicting factors: the electrophilicity of the resulting ring-opened "protonated carbocation" (which substituents influence in just the reverse manner to how they influence initiation), the accessibility of the negative EMPC map around the ring oxygen (the EMPC map is related to the basicity of the oxygen) and steric hindrance to attack on the ring oxygen. There have been a few experimental studies on relative polymerization ratios in this overall Navy project, but to date these partners have been picked for their relevance to the actual polymers being synthesized. However, these monomers have not been picked to make a coherent series for comparison to theory. We have had continuing fruitful detailed discussions with Gerald Manzer, who is synthesizing a number of monomers and polymers. A few well-defined experiments could help disentangle some of the conflicting and complicating factors in the propagation step. Manzer indicated to us in June and again in recent conversations that he will be carrying out some fundamental studies of cationic copolymerization with standards such as oxetane to have a set of coherent results for meaningful correlations of copolymerization ratios.

In a copolymerization experiment monomers 1 and 2 must first undergo initiation. Hence, for a preliminary attempt to compare our calculated theoretical indices with experimentally measured copolymerization reactivity ratios, we considered our EMPC maps, which are indicative of basicity and hence of propensity of a monomer to initiate (or preference of a monomer to be attacked by a propagating species).

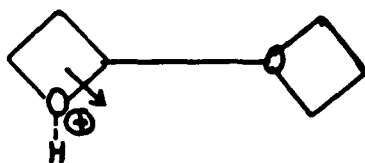
Formation of random copolymers are determined by the selectivity of the propagation reaction, i.e. the relative reactivities of the comonomers. However, it has been shown experimentally for copolymerization of more conventional species that relative monomer reactivities on the copolymerization may differ strongly from the apparent monomer reactivities in homopolymerization. A species which is less reactive in homopolymerization may be the preferentially consumed comonomer in the cationic copolymerization. This complicates greatly the prediction of relative polymerization ratios for copolymerization.

We are also considering some additional theoretical approaches to understanding the propagation step.

Recently, Gerry Manzer, Dr. Lillya and Dr. Bob Earl have suggested to us that rather than a ring-opened "protonated carbocation", more direct attacks might take place.

The propagation step might be more complicated than ring opening of the "protonated carbocation" and subsequent attack of the ring opened "protonated carbocation" on the second molecule of monomer. Rather, they hypothesized that there might be an attack of the "protonated carbocation" on the second molecule of monomer with a concomitant ring-opening.

Manzer suggested:

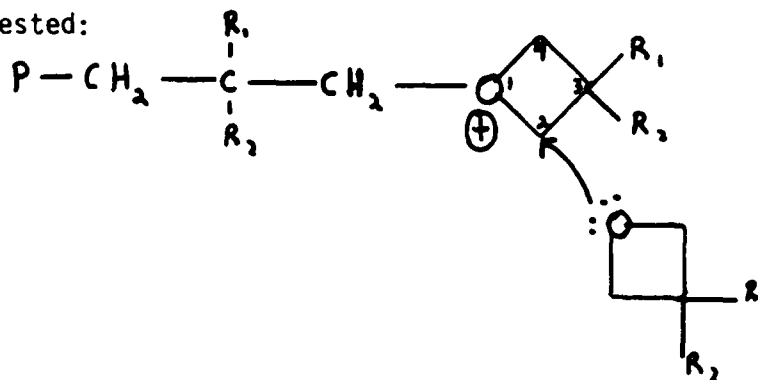


Lillya suggested essentially the same overall picture:



since he does not think that the ring-opened "protonated carbocation" forms because 1° carbocations do not form except under very rare circumstances and are not very stable.

Earl suggested:



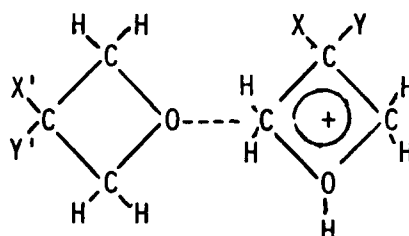
To investigate this particular mechanism will necessitate doing ab-initio MRD-CI or CASSCF calculations since a bond is being broken. Since the system of "protonated carbocation" plus a second molecule of monomer is large, the most rational approach on this generation CRAY-1 or CRAY-XMP supercomputers is to carry out MRD-CI or CASSCF calculations on localized molecular orbitals in the region of the attack process, with the remainder of the occupied molecular orbitals being folded into an effective CI Hamiltonian.

As a preparation for future CASSCF (complete active space multiconfiguration SCF) calculations on the attack of a "protonated carbocation" on another molecule of monomer using localized orbitals, we carried out CASSCF calculations using localized orbitals on a prototype oxetane, FNOX (3-fluoro-3-nitrooxetane). These CASSCF results were well-behaved which is encouraging.

We initiated preliminary CASSCF calculations of the ring opening process of oxetane and protonated oxetane starting with localized orbitals. However, the CASSCF procedure (which is an iterative MC-SCF calculation) turns out to delocalize the molecular orbitals again to an extent which makes it unrealistic to analyze these results in terms of localized orbitals.

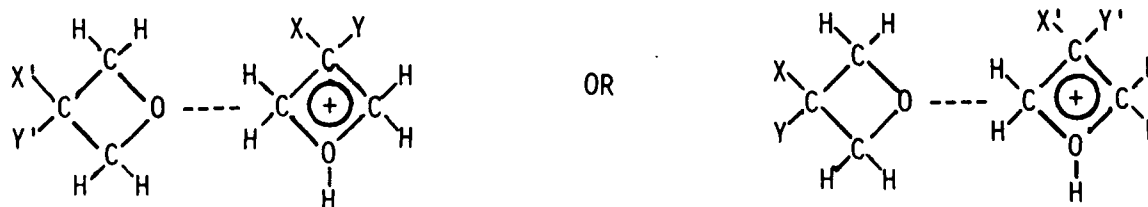
Thus we initiated preliminary MRD-CI calculations on opening the oxetane and protonated oxetane rings in preparation for an investigation of

the mechanism of the propagation step in cationic polymerization. Both ab-initio MODPOT and ab-initio all-electron valence double zeta MRD-CI calculations were carried out to investigate basis set dependence. The results indicated that the potential energy surfaces resembled each other whether only localized orbitals in the region of the bond being broken or whether the full set of canonical molecular orbitals were used in the MRD-CI. So far the MRD-CI potential energy surfaces have been investigated with ab-initio MODPOT or an ab-initio all-electron valence double zeta basis sets. Further basis sets will be investigated but these initial results are very encouraging. The preliminary all-electron MRD-CI results indicate that it takes less energy to open the protonated oxetane ring than the ring of neutral oxetane. We are now carrying out preliminary ab-initio MODPOT/VRDDO/MERGE MRD-CI calculations for opening the protonated oxetane ring in the presence of another attacking oxetane molecule.



This investigation uses our strategy of explicit MRD-CI calculations on the localized orbitals in the region of the bond with the remainder of the occupied molecular orbitals being folded into an effective CI Hamiltonian.

This study of opening the protonated oxetane ring while a second oxetane molecule is attacking is an excellent illustration of the power and versatility of the various programs which we have meshed together and gotten operational on the CRAY'S. Without using our ab-initio MODPOT/VRDDO/MERGE procedure the integral times would become very large for higher X and Y substituents and for the number of geometries that would have to be investigated. Without carrying out the MRD-CI calculations based on localized orbitals in the region of the bond being opened, the MRD-CI calculations would be intractable in this generation of CRAY 1 or CRAY XMP computers. However, the localized orbital MRD-CI approach looks extremely promising for investigating the propagation step of the substituted oxetanes. With this technique we should be able to gain insight into such questions as will the propagation step in copolymerization (where X and X' are different and Y and Y' are different) prefer to go



This same series of computer programs is also being and will continue to be used for bond breaking problems on dissociation of energetic molecules and as building blocks for a sequence of programs to calculate input data for fractoemission calculations and for calculations on fractoemission processes.

We had originally intended to carry out the calculations for this oxetane propagation step investigation on the NRL CRAY XMP-12 as soon as we got all of the necessary program pieces converted and meshed together. The very initial studies were carried out on the NRL CRAY XMP-12. However in view of the severely limited amount of computer time allotted to us on the NRL CRAY, we had to spend time again to convert the entire meshed program sequence to another CRAY where a more realistic amount of computer time is available. This conversion was accomplished and the calculations are well underway.

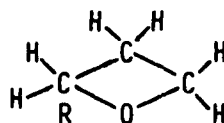
AB-INITIO MULTIREFERENCE DOUBLE EXCITATION CONFIGURATION INTERACTION

MRD-CI

1. DO A MODEST CI CALCULATION (SEVERAL THOUSAND CONFIGURATIONS).
2. FROM THESE PICK THE MOST IMPORTANT (USUALLY ~ 20).
3. ALLOW ALL SINGLE AND DOUBLE EXCITATIONS FROM ALL REFERENCE DETERMINANTS (GENERATES ~ 750,000 CONFIGURATIONS).
4. ESTIMATE THE ENERGY CONTRIBUTION OF EACH OF THE ~ 750,000 CONFIGURATIONS BY A PERTURBATIVE PROCEDURE.
5. SET A THRESHOLD. DO CI EXPLICITLY FOR CHOSEN CONFIGURATIONS.
6. ADD BACK IN THE ENERGIES OF OTHER CONFIGURATIONS BY PERTURBATIVE PROCEDURE AND EXTRAPOLATE.
7. ADD DAVIDSON TYPE CORRECTION FOR SIZE CONSISTENCY.

$$E_{(\text{FULL CI})} = E_{(\text{EXT})} + (1 - \sum_p^{\text{ref}} C_p^2 [E_{(\text{EXT})} - E_{(\text{REF})}])$$

The following tables present examples of the types of information which result from our MRD-CI calculations on opening the oxetane ring.



The MRD-CI calculations were run from $R = 2.8$ a.u. [equilibrium geometry - the undistorted oxetane (or protonated oxetane) ring] to 4.9 a.u. [the opened oxetane (or protonated oxetane) ring].

Tables I-IV present the number of active orbitals in the MRD-CI, which specific localized molecular orbitals were included in the MRD-CI, the E_{SCF} , E_{EXT} , E_{full} and the coefficients (c^2) of the dominant configurations in the final MRD-CI wave function. For these initial test calculations, both our ab-initio MODPOT basis was used (valence electrons only) as well as a more conventional Dunning 3^S3^P contraction of a Huzinaga 9^S5^P atomic basis set.

Table I	Oxetane	(R = 2.8 a.u.)	MRD-CI
Table II	Oxetane	(R = 4.9 a.u.)	MRD-CI
Table III	Protonated Oxetane	(R = 2.8 a.u.)	MRD-CI
Table IV	Protonated Oxetane	(R = 4.9 a.u.)	MRD-CI

Tables V-VIII present the energies (E_{SCF} , E_{CI} , E_{EX} and E_{full}) and the dominant configurations in the final MRD-CI wave functions of oxetane and protonated oxetane as a function of R.

Table I

OXETANE	(equilibrium geometry	R = 2.8 a.u.)	MRD-CI	Energies (a.u.)
MODPOT Basis				
Dunning (3s2p) basis				
16 active orbitals				
4 occupied orbitals				
localized	1	01a (lone pair)	5	C3C401*
orbitals	2	01C4	6	C3C201*
	3	01C2	7	C4H01*
	4	01b (lone pair)	8	C201*
	5	01C4*	9	C3C401*
	6	01C2*	10	C401*
			11	01a* (lone pair)
			12	C201*
			13	C3C401*
			14	C3C201*
			15	C3C201*
			16	01* (lone pair)
$E_{SCF} = -35.499798$				
$E_{CI} = -35.560066$				
$\Delta E_{CI} = -.062028$				
$E_{EX} = -35.560883$				
$\Delta E_{EX} = -.061085$				
$\Delta E_{Full} = -35.560962$				
$\Delta E_{Full} = -.061164$				
$E_{SCF} = -191.413135$				
$E_{CI} = -191.530561$				
$\Delta E_{CI} = -.117426$				
$E_{EX} = -191.533677$				
$\Delta E_{EX} = -.120542$				
$E_{Full} = -191.536176$				
$\Delta E_{Full} = -.123041$				
reference functions	c^2	reference functions		
GS	.960	GS		
(01C4) ² + (01C4*) ²	.014	(01C4) ² + (01C4*) ²		
(01C2) ² + (01C2*) ²	.014	(01C2) ² + (01C2*) ²		
(01a) + (01C2*)	.0001	(01a) + (01a*)		
(01b) + (01C2*)	.0001	(01b) + (01b*)		
(01C2) + (01C4) + (01C2*) + (01C4*)	.004	(01C4) + (01C2) + (01C4*) + (01C2*)		
		.957		
		.007		
		.007		
		.00003		
		.00003		
		.0012		

Table II

OXETANE	(open ring	R = 4.9 a.u.)	MRD-CI	Energies (a.u.)
MODPOT Basis				
6 active orbitals				
4 occupied orbitals				
			Dunning (3s2p) basis	
			17 active orbitals	
			4 occupied orbitals	
localized orbitals	1 01A (lone pair)	localized orbitals	1 01a (lone pair)	7 C2H01*
	2 01C2		2 01C2	8 C2C301*
	3 01b (lone pair)		3 01b (lone pair)	9 C2H01*
	4 01C4		4 01C4	10 C4H01*
	5 01C4*		5 01C4*	11 C4H01*
	6 01C2*		6 C2H01*	12 01C2 _I *
				13 C2H01*
				14 01C2 _{II} *
				15 01a* (lone pair)
				16 01b* (lone pair)
				17 01C2* (1s)
E_{SCF} = -35.296436		E_{SCF} = -191.226115		
E_{CI} = -35.477720	ΔE_{CI} = -.181284	E_{CI} = -191.373828	ΔE_{CI} = -.147713	
E_{EX} = -35.477799	ΔE_{EX} = -.181363	E_{EX} = -191.377880	ΔE_{EX} = -.151765	
E_{Full} = -35.478426	ΔE_{Full} = -.182050	E_{Full} = -191.379861	ΔE_{Full} = -.153746	
reference functions	c^2	reference functions	c^2	
GS	.702	GS	.784	
(01C4) ² + (01C4*) ²	.230	(01C4) ² + (01C4*) ²	.094	
(01C2) ² + (01C2*) ²	.011	(01C2) ² + (01C2*) ²	.006	
(01C4) + (01C4*)	.008	(01C4) + (01C4*)	.038	
(01C2) + (01C2*)	.0002	(01C2) + (01C2*)	.0002	
(01a) + (01C4) + (01C4*) ²	.011	(01a) + (01C4) + (01C4*) ²	.014	
(01b) + (01C4) + (01C4*) ²	.011	(01b) + (01C4) + (01C4*) ²	.014	
(01C2) + (01C4) + (01C2*) + (01C4*)	.004	(01C2) + (01C4) + (01C2*) + (01C4*)	.003	

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Table III

PROTONATED OXETANE	H ⁺ head on (equilibrium geometry R = 2.8 a.u.)				MRD-CI	Energies (a.u.)
Dunning (3s2p) basis						
MODPOT Basis		18 active orbitals 4 occupied orbitals				
7 active orbitals 4 occupied orbitals	localized orbitals	1 01H ⁺	2 01C4	3 01 (lone pair)	4 01C2	5 01C4*
		6 01C2*	7 01H ⁺ *			
	</					

Table IV

PROTONATED OXETANE	H ⁺ head on (open ring R = 4.9 a.u.)	MRD-CI	Energies (a.u.)
Dunning (3s2p) basis			
18 active orbitals			
4 occupied orbitals			
Dunning (3s2p) basis			
18 active orbitals			
4 occupied orbitals			
localized orbitals	1 01H ⁺	2 C2H01*	15 C3C40*
2 01C2	3 01a (lone pair)	9 C3C201*	16 01C2*
3 01a (lone pair)	4 01b (lone pair)	10 C4H01*	17 C3C201*
4 01b (lone pair)	5 C3C401*	11 01C2H ⁺ *	18 01b* (lone pair)
5 01C4*	6 01H _I ⁺ *	12 01C2H ⁺ *	
6 01C2*	7 C4H01 ⁺ *	13 01a* (lone pair)	
7 01H ⁺ *		14 01H _{II} ⁺ *	
E _{SCF} = -191.644291			
E _{CI} = -191.759479 ΔE _{CI} = -.115188			
E _{EX} = -191.764075 ΔE _{EX} = -.119784			
E _{FULL} = -191.766711 ΔE _{FULL} = -.122420			
reference functions			
GS			c ²
(01H ⁺) ² → (01H ⁺ *) ²			.9622
(01C2) ² → (01C2*) ²			.0028
(01H ⁺) → (01H ⁺ *)			.0062
(01C2) → (01C2*)			.00003
(01H ⁺) + (01C2) → (01H ⁺ *) + (01C2*)			.000029
(01H ⁺) + (01C2) → (01H ⁺ *) + (01C2*)			.0003
E _{SCF} = -35.695881			
E _{CI} = -35.747250 ΔE _{CI} = -.051369			
E _{EX} = -36.278284 ΔE _{EX} = -.582403			
E _{FULL} = -36.282775 ΔE _{FULL} = -.582403			
reference functions			
GS			c ²
(01H ⁺) ² → (01H ⁺ *) ²			.968
(01C2) ² → (01C2*) ²			.008
(01a) + (01C2) → (01C2*) ²			.013
(01b) + (01C2) → (01C2*) ²			.0004
(01H ⁺) + (01C2) → (01H ⁺ *) + (01C2)			.0004
(01H ⁺) + (01C2) → (01H ⁺ *) + (01C2)			.002

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Table V

OXETANE	MODPOT Basis	MRD-CI			
R(01-C4) a.u.	2.8	3.4	3.9	4.4	4.9
E _{SCF}	-35.49979	-35.47147	-35.41497	-35.35475	-35.29643
E _{CI}	-35.56007	-35.55239	-35.52337	-35.49624	-35.47772
E _{EX}	-35.56008	-35.55256	-35.52345	-35.49698	-35.47780
E _{Full}	-35.56096	-35.55267	-35.52364	-35.49729	-35.47848
Σc^2	.9931	.9911	.9878	.9839	.9698
Ground state	.9601	.9293	.8759	.7998	.7021
(01C2) \rightarrow (01C2*)	.0143	.0138	.0128	.0117	.0107
(01C4) ² \rightarrow (01C4*) ²	.0143	.0372	.0816	.1492	.2358
(01C4) + (01C2) \rightarrow (01C4*) + (01C4*)	.0039	.0049	.0051	.0046	.0040

c^2 for the most important configurations

OXETANE	Dunning [3 ^s 2 ^p] Basis	MRD-CI
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Basis H. J. Dunning, Jr., P. J. Hay in *Methods of Electronic Structure Theory III*, Ed. H. F. Schafer III, pl. 27. Contracted from Huzinaga's (95^b) basis

c' for the most important configurations

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Table VII

PROTONATED OXETANE (head on) MODPOT BASIS					MRD-CI
R [a.u.]	2.8	3.4	3.9	4.4	4.9
E_{SCF}	-35.80659	-35.78903	-35.75085	-35.71924	-35.69588
E_{CI}	.86933	.85636	.81591	.77709	.74725
E_{EX}	.86957	.85667	.81608	.77773	-36.27828
E_{Full}	.86968	.85688	.81634	.77799	136.28277
Σc^2	.9932	.9898	.9877	.9868	.9917
Ground state	.9685	.9592	.9537	.9583	.9682
(01C 2)+(01C2*)	.0075	.0084	.0096	.0114	.0135
(01C4)+(01C4*)	.0075	.0106	.0087	.0021	.0000
(01H ⁺)+(01H ⁺⁺)	.0056	.0060	.0062	.0071	.0081
(01C2) + (01C4) +(01C2*) + (01C4*)	.0026	.0035	.0041	.0031	.0020

c^2 for the most important configurations

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Table VIII

PROTONATED OXETANE	Dunning ($3^5 2^P$) Basis	MRD-CI			
R (01C4) a.u.	2.8	3.4	3.9	4.4	4.9
E_{SCF} (a.u)	-191.75741	-191.72955	-191.68723	-191.66533	-191.64429
E_{CI}	.86992	.84796	.80646	.77691	.75948
E_{EX}	.87250	.85259	.81071	.78166	.76407
E_{Full}	.87454	.85588	.81440	.78481	.76671
Σc^2	.9735	.9696	.9657	.9701	.9682
Ground state	.9651	.9598	.9589	.9641	.9622
(01C2) + (01C2*)	.0037	.0042	.0043	.0058	.0062
(01C4) + (01C4*)	.0037	.0039	.0030	.0000	.0000
(01C4) + (01C2) + (01C4*) + (01C2*)	.0008	.0010	.0000	.0000	.0000

c^2 for the most important configurations

This past year we also carried out some additional quantum chemical calculations and generated EMPC maps for substituted oxetanes. The oxetanes we investigated were:

BMNAMO 3,3-bis(methylnitraminomethyl)oxetane
for both the experimental crystal structure, which had
a puckered oxetane ring, and for a planar oxetane ring,
which was the lower in calculated total energy.

MMNAMO 3-methyl-3(methylnitraminomethyl)oxetane
for both a puckered oxetane ring (as in the crystal
structure of MNBMNAMO) and for a planar oxetane ring,
which again was lower in total calculated energy.

We will still be carrying out more calculation for optimization of geometries of these molecules since these compounds have multiple maxima and minima.

These oxetanes with the floppy substituents have multiple maxima and minima. Thus merely optimizing geometries with any customary derivative method can only lead to a local minimum dependent on the starting geometry. We plan to give attention to developing a program strategy which will combine our ab-initio MODPOT/VRDDO/MERGE technique with derivatives. Our recent MRD-CI calculations on oxetane and protonated oxetane with both ab-initio MODPOT and ab-initio all electron double zeta atomic basis sets indicate the reliability of the ab-initio MODPOT atomic basis sets which can be used for the vast majority of geometry optimizations of oxetanes.

III. MRD-CI Calculations on Decomposition Pathways of Energetic Nitrocompounds

A. Nitrobenzene

The dissociation of $>C - NO_2$ and $>N - NO_2$ bonds of nitroexplosives are one of the key primary steps in initiation of explosives. It had been suggested recently that in nitroexplosives where the potential energy surfaces for ground or electronically excited states indicated that one or more of the dissociative pathways could undergo predissociation, these predissociative pathways could lead to products with sizable amounts of kinetic energy, thus initiating processes leading to detonation in the crystal. The molecular decomposition pathways of the nitroexplosives and the initiation and subsequent steps in detonation would then be completely intertwined. To study molecular decomposition pathways it is necessary to use ab-initio MRD-CI (multireference determinant-configuration interaction) or CASSCF (complete active space multiconfiguration SCF) calculations. Our previous MRD-CI and CASSCF results on the $>C - NO_2$ decomposition of nitromethane and our MRD-CI calculations on the $>N - NO_2$ decomposition pathway of RDX had indicated that there were multiconfiguration electronic wave functions even in the ground electronic state at equilibrium geometry and additional configurations along the dissociation pathway. Because the nitroexplosives are large molecules, it is still computationally rather intractable computer space and time wise to carry out CI calculations for the entire molecule. By localizing and focusing on the $>C - NO_2$ or $>N - NO_2$ decomposition pathway, much important insight can be gained about how many and what kind of potential energy surfaces are involved, and to what types of product species they lead. This MRD-CI method, which also includes techniques to account for linked double excitations, is also applicable to intermolecular interactions. The most rational strategy on this generation of CRAY-1 or CRAY-XMP supercomputers is to carry out the MRD-CI or CASSCF calculations on localized or local molecular orbitals in the region of the bond being broken (either strictly orthogonal localized orbitals or canonical orbitals in that region of space) with the remainder of the occupied molecular orbitals being folded into an effective CI Hamiltonian.

For our initial studies on the $>C - NO_2$ decomposition pathway of nitrobenzene we carried out ab-initio all-electron MRD-CI calculations with a $10^5 6P + 3^5 2P$ basis set on the C, N, O, atoms and a $3^S + 1^S$ basis on the H atoms. There were a total of 50 molecular orbitals (32 occupied and 18 virtual). While we have carried out ab-initio strictly orthogonal localized orbital MRD-CI calculations for the bond dissociation of aliphatic nitrocompounds (such as RDX), it is not completely unambiguous how to best to localize molecular orbitals for an aromatic system. Thus we carried out the MRD-CI calculations on nitrobenzene using canonical molecular orbitals taking explicit account in the MRD-CI of the occupied molecular orbitals in this region of the $\overset{C}{>C} - NO_2$ bond being dissociated (15 occupied molecular orbitals) and all of the virtual orbitals. The other 17 of the occupied molecular orbitals were folded into an effective CI Hamiltonian.

Table IX presents for the 1A_1 , 3A_1 , 1A_2 , 3A_2 , 1B_1 , 3B_1 , 1B_2 and 3B_2 states of nitrobenzene the number of reference configurations, the total number of configurations generated, the number of configurations selected (by the perturbative procedure with a threshold of 30 μ H).

Table IX

NITROBENZENE MRD-CI NUMBER OF CONFIGURATIONS ($R_{C-N} = 2.8$ A.U.)

STATE	NO. OF REFERENCE CONFIGURATIONS	NO. OF CONFIGURATIONS GENERATED	NO OF CONFIGURATIONS SELECTED
1A_1 (GS)	8	40662	2651
3A_1	17	576557	2094
1A_2	17	98609	2060
3A_2	17	98604	2094
1B_1	16	90255	2040
3B_1	8	45748	2010
1B_2	20	111563	2038
3B_2	16	87816	2106

THRESHOLD $30\mu H$

As with the dissociation of other $>\text{C} - \text{NO}_2$ or $>\text{N} - \text{NO}_2$ compounds, there is a crossing of molecular orbitals along the dissociation pathway (Figure 1). The surfaces for E_{CI} , E_{EXT} and E_{full} are all essentially parallel (Figure 2).

Our MRD-CI results on the $^1\text{A}_1$, $^3\text{A}_1$, $^1\text{A}_2$, $^3\text{A}_2$, $^1\text{B}_1$, $^3\text{B}_1$, $^1\text{B}_2$ and $^3\text{B}_2$ states of nitrobenzene show a wealth of structure in the potential energy surfaces for the various electronic states of nitrobenzene as a function of $>\text{C} - \text{NO}_2$ distance. (Figure 3)

MOLECULAR ORBITAL ENERGIES (a.u.) FOR NITROBENZENE AS A FUNCTION OF R_{CN} (a.u.)

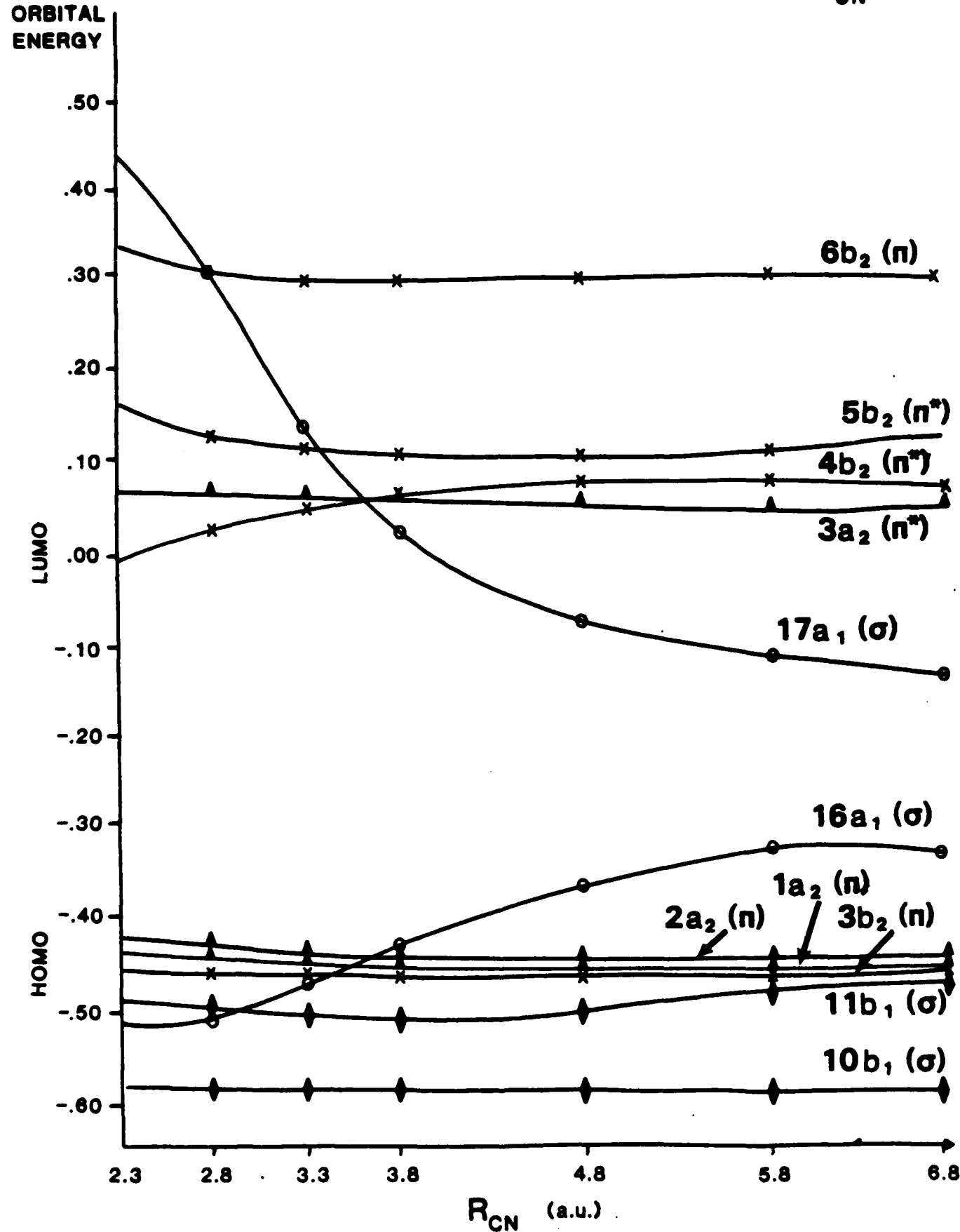
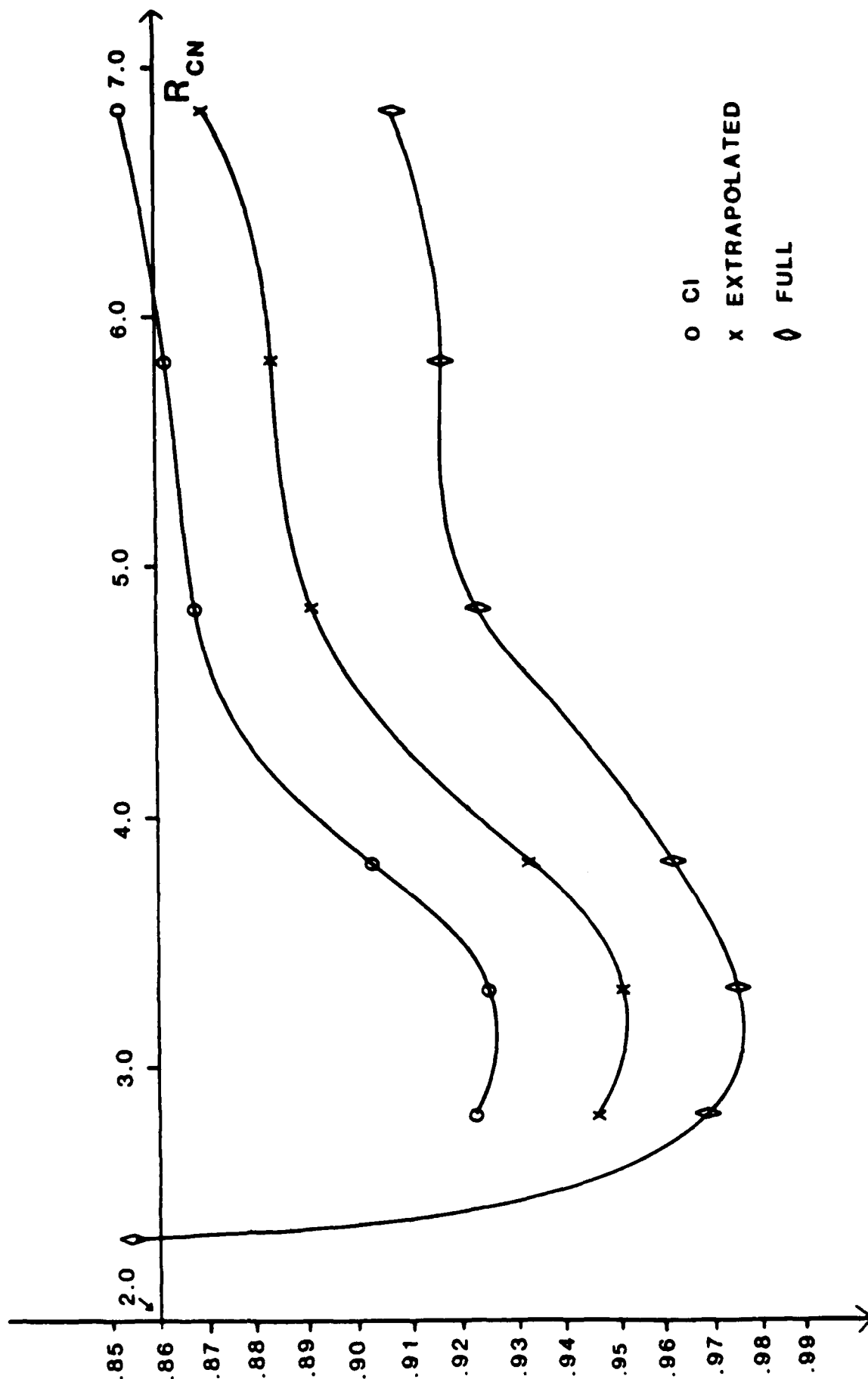


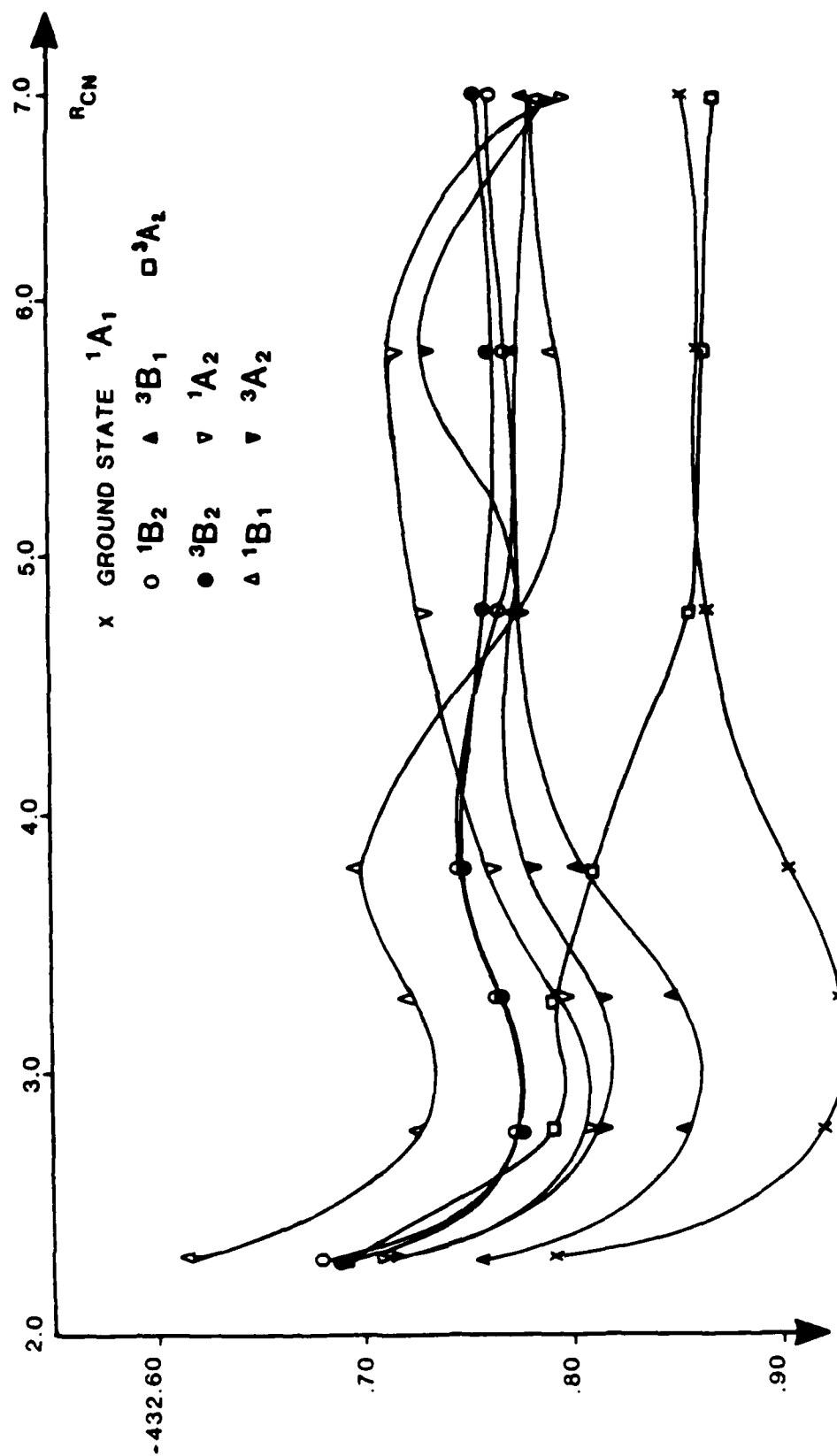
Figure 1

NITROBENZENE MRD-CI GROUND STATE (1A_1) ENERGIES (a.u.) vs. R_{CN} (a.u.)

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Figure 2



NITROBENZENE MRD-CI EXTRAPOLATED CI ENERGIES (a.u.) vs. R_{CN} (a.u.)
MINIMAL BASIS



It is obvious from examination of the potential energy surfaces in Figure 3 that there are a number of potential energy surfaces which exhibit surface crossing behavior and some which even exhibit predissociative behavior. To verify these apparent surface crossings, the c^2 for the dominant configurations in the final MRD-CI calculation for each different surface at each R_{C-N} are presented in Tables X-XVII. Examination of Table

X (the ground electronic state 1A_1) shows that even at equilibrium geometry there is still the contribution of the excitation

$$(\pi)^2 \rightarrow (\pi^*)^2[(1a_2)^2 \rightarrow (4b_2)^2]$$

in the NO_2 group (as in nitromethane). Also, the results in Table X verify that a number of other configurations become important along the dissociation pathway even of the ground electronic state. For some of the higher states which exhibit surface crossings it can be seen that at points corresponding to surface crossings there is a complete change in the dominant configurations in the wave functions.

By monitoring the dominant configurations of the various molecular orbital fillings as a function of $>C - NO_2$ distance it is possible to determine accurately how many times a particular potential energy surface changes dominant configuration. The ground 1A_1 state is not predissociative. However, the relative contributions of the various determinants change as a function of $>C - NO_2$ distance (Table X). The 3A_1 state is predissociative (Table XI). Both the 1A_2 and 3A_2 states are predissociative and both change dominant configuration at least twice along their potential energy surfaces. (Tables XII and XIII)

The 1B_1 state is predissociative and changes dominant configuration at least once along its potential energy surface (Table XIV).

The 3B_1 state is very slightly predissociative, changing dominant configuration at least once along its potential energy surface (Table XV).

The 1B_2 and 3B_2 surfaces are predissociative, each changing dominant configuration at least twice along their potential energy surfaces (Tables XVI and XVII).

NITROBENZENE MRD-CI MAIN REFERENCE FOR THE GROUND ELECTRONIC STATE C_2^2

R_{CN} (a.u.)

STATE	2.3	2.8	3.3	3.8	4.8	5.8	6.8
G.S.	.839	.841	.832	.798	.656	.522	.449
$(1a_2)^2 \rightarrow (4b_2)^2$.010	.008	.007	.005	.000	.000	.000
$(16a_1)^2 \rightarrow (17a_1)^2$.000	.001	.008	.031	.153	.274	.357
$(1a_2)^2 \rightarrow (5b_2)^2$.001	.002	.006	.012	.018	.015	.000
$(2a_2)^2 \rightarrow (3a_2)^2$.002	.003	.007	.011	.010	.008	.000
$(1a_1)^2 \rightarrow (4b_2) + (5b_2)$.003	.003	.010	.015	.003	.000	.000
$(16a_1) \rightarrow (17a_1)$.000	.000	.002	.007	.027	.042	.050

NITROBENZENE C^2 FOR MAIN REFERENCE CONFIGURATIONS 3A_1

	CONFIGURATIONS	2.3	2.8	3.3	3.8	4.8	5.8	6.8
I	(3b ₂) → (4b ₂)	.425	.241	.185				
	(2a ₂) → (3a ₂)	.134	.254	.474				
	(1a ₂) → (3a ₂)	.190	.250	.073				
	(16a ₁) → (17a ₁)				.844	.852	.853	.851

1A_2 SINGLET MAIN REFERENCE C^2

	R	2.3	2.8	3.3	3.8	4.8	5.8	6.8
CONFIGURATION	$(11b_1) \rightarrow (4b_2)$.702	.611	.501	.343	.406	.001	—
	$(11b_1) \rightarrow (5b_2)$.081	.199	.327	.466	.626	.537	—
	$(16a_1)^2 + (11b_1)^2 \rightarrow$ $(5b_2) + (17a_1)$	—	—	—	—	.116	.246	—
	$(16a_1) + (2a_2) \rightarrow (17a_1)^2$	—	—	—	—	—	—	.274
	$(2a_2) \rightarrow (17a_1)$	—	—	—	—	—	—	.561

3A_2 TRIPLET MAIN REFERENCE C^2

	R	2.3	2.8	3.3	3.8	4.8	5.8	6.8
CONFIGURATION	$(11b_1) \rightarrow (4b_2)$.710	.618	.493	.348	.046	.001	—
	$(11b_1) \rightarrow (5b_2)$.094	.210	.346	.467	.604	.502	—
	$(16a_1)^2 + (11b_1) \rightarrow$ $(5b_2) + (17a_1)^2$	—	—	—	—	.123	.244	—
	$(16a_1) + (2a_1) \rightarrow (17a_1)^2$	—	—	—	—	—	—	.273
	$(2a_2) \rightarrow (17a_1)$	—	—	—	—	—	—	.562

NITROBENZENE MAIN REFERENCE C² FOR SINGLET ¹B₁

	R	2.3	2.8	3.3	3.8	4.8	5.8	6.8
CONFIGURATION	(3b ₂) → (3a ₂)	.168	.353	.434	.456	—	—	—
	(4b ₂) → (2a ₂)	.488	.261	.231	.250	—	—	—
	(11b ₁) → (17a ₁)	—	—	—	—	.632	.541	.551
	(16a ₁) + (11b ₁) → (17a ₁)	—	—	—	—	.172	.235	.257

NITROBENZENE MAIN REFERENCE C² FOR TRIPLET ³B₁

	R	2.3	2.8	3.3	3.8	4.8	5.8	6.8
CONFIGURATION	(4b ₂) → (2a ₂)	.486	.349	.129	.005	—	—	—
	(4b ₂) → (1a ₂)	.256	.290	.384	.353	—	—	—
	(5b ₂) → (1a ₂)	.046	.112	.285	.471	—	—	—
	(17a ₁) → (11b ₁)	—	—	—	—	.661	.588	.556
	(16a ₁) + (11b ₁) → (17a ₁)	—	—	—	—	.150	.226	.264

NITROBENZENE MAIN REFERENCE C^2 FOR LOWEST 1B_2

	R	2.3	2.8	3.3	3.8	4.8	5.8	6.8
CONFIGURATION	$(16a_1) \rightarrow (4b_2)$.686	.641	.582	.385	.036	.001	.001
	$(16a_1) \rightarrow (5b_2)$.087	.187	.259	.397	.463	.368	.320
	$(16a_1)^2 \rightarrow (17a_1) + (5b_2)$	—	—	—	—	.318	.461	.512

NITROBENZENE MAIN REFERENCE C² FOR LOWEST ³B₂

	R	2.3	2.8	3.3	3.8	4.8	5.8	6.8
CONFIGURATION	(16a ₁) → (4b ₂)	.686	.641	.582	.385	.036	.001	.001
	(16a ₁) → (5b ₂)	.087	.187	.259	.397	.463	.368	.140
	(16a ₁) → (17a ₁) + (5b ₂)	—	—	—	—	.318	.461	.512

Thus nitrobenzene and other nitroaromatic explosives will have a multitude of possible predissociative pathways.

Hence, in summary, it is apparent that detailed MRD-CI calculations such as we report here will be necessary to describe the properties and dissociation of both ground and excited electronic states of nitroexplosives. This will be especially crucial in understanding initiation of detonation as well as subsequent steps.

We are continuing these studies to identify the structures of the higher lying potential energy surfaces. In order to calculate the higher roots, the program dimensions will have to be enlarged to handle a) more reference configurations, b) more active electrons and c) to pull even more higher eigenvalues from the large CI matrix than the program now does. The increase in these dimensions will be important for research on any larger energetic compounds.

IV. POLY-CRYST

The POLY-CRYST program (for ab-initio calculations on crystals and polymers) has been converted to the CRAY-1M and to the CRAY-XMP. We initiated preliminary timing test calculations on a system of three unit cells of nitromethane (four molecules per unit cell). As with the quantum chemical calculations of many nitrocompounds, the crystal orbital SCF calculation of nitromethane is difficult to converge. Using the special extrapolation and damping techniques we had developed over the years, we converged this calculation. However, even on a CRAY-XMP, calculation of the three unit cell system on nitromethane is not trivial timewise, even using a minimal atomic basis set, ab-initio effective core model potentials for the inner shells and our charge conserving integral prescreening evaluation. The calculation for one unit cell of nitromethane (integrals and SCF) took 120 seconds. For the three cell system the integrals took 400 seconds, and the complex SCF for 20 iterations but only six \vec{k} points (since the three cells were linear) took 1100 seconds. We will systematically be increasing the number of unit cells. At the least, 27 unit cells should be run for this problem. For a three-dimensional system one may have to use 50-100 \vec{k} points. We will be investigating this as well as whether long range effects have to be included for molecular crystals and, if so, the best way to include them.

Because of the size of the nitroexplosive molecules and the large number of molecules in a unit reference cell (as high as 8 for RDX), the full power of our POLY-CRYST program for nitroexplosives will only reach fruition on the next generation of CRAY-2 type supercomputers. (CRAY-2 computers, which have a CPU core memory of 256 million real 64-bit words, have already been delivered. This compares to the only two million to eight million words of CPU memory on the current CRAY-XMP's.) We are poised and ready for the next generation of supercomputers.

V. Ab-initio Atom Class - Atom Class Potential Functions and Prediction of Crystal Densities

In addition to being useful in predicting optimum crystal unit cell parameters for energetic molecules, these ab-initio atom class - atom class potential functions can be used to gain insight into the bonding and arrangement of such molecules in clusters and the interactions of such molecules both in gas and condensed phases. Such potentials can provide valuable input for molecular dynamics and hydrodynamics modeling.

We converted to the CRAY-XMP our programs necessary for these studies:

INTER-MOLASYS for ab-initio intermolecular SCF calculations with energy partitioning to obtain atom class-atom class ab-initio potential energy functions and correction for basis set superposition error (BSSE).

CRYSTAL-JHU for optimizing unit cell parameters.

We have derived and implemented procedures to calculate ab-initio atom class-atom class potentials from energy partitioned ab-initio SCF calculations between molecules and to use these potentials plus dispersion energy to optimize crystal unit cell parameters (from which densities are calculated).

There are a number of terms in our expression for the intermolecular energy in a crystal. The main components of the two-body interaction energy are

$$E = E_{EL}^{(1)} + E_{EX}^{(1)} + E_{IND}^{(2)} + E_{DISP}^{(2)} \quad (1)$$

The first three contributions to equation 1 can be obtained from the decomposition of the variational E_{SCF} interaction energy corrected for basis set superposition error (BSSE).

We had also developed procedures to calculate the $E_{EL,MTP}$ (the electrostatic contribution from the atomic multipole moments) and the $E_{IND,LE}$ (the long range induction) explicitly each time for each arrangement of molecules. The short range terms $E_{EL,PEN}$, E_{C-T} , $E_{IND,CT}$ are fitted to functional forms. The dispersion terms are estimated semi-theoretically. We initiated considering additional approaches to calculating these potentials (especially the dispersion contributions which contribute a significant fraction of the intermolecular interaction energy even for nitroexplosives which also have strong charge redistribution and hence strong electrostatic and inductive contributions to the intermolecular interaction energy).

VI. Lectures Presented On This ONR Research

Presentations given and/or scheduled and papers published and/or submitted during the fiscal year

A. Presentations Given Dr. Joyce J. Kaufman

1. Already presented (* denotes invited lecture)

a. National and International Meetings

- * "CI Calculations on the Decomposition of RDX Based on Localized Orbitals," Sanibel International Symposium on Quantum Chemistry, Solid-State Theory, Many-Body Phenomena, and Computational Quantum Chemistry, Marineland, Florida, March 1985.

- * "MRD-CI and CASSCF Calculations on the Decomposition Pathway of Nitromethane," Sanibel International Symposium on Quantum Chemistry, Solid-State Theory, Many-Body Phenomena, and Computational Quantum Chemistry, Marineland, Florida, March 1985.

POLY-CRYST - A Program for Ab-Initio Crystal Orbitals and Polymer Orbitals," International Conference on the Theory of the Structures of Non-Crystalline Solids, Bloomfield Hills, Michigan, June 1985.

- * "Ab-Initio MODPOT/VRDDO/MERGE Multireference Determinant Configuration Interaction (MRD-CI) Calculations for the $\text{>N} - \text{NO}_2$ Decomposition Pathway of RDX Based on Localized Orbitals," 5th International Congress of Quantum Chemistry, Montreal, Canada, August 1985.
- * "Ab-Initio CASSCF and Multireference Determinant Configuration Interaction (MRD-CI) Calculations on Energetic Compounds," NATO Advanced Study Institute on Chemical Reaction Dynamics, Crete, Greece, August 1985.
- * "Prediction of Crystal Structures of Energetic Compounds Using Ab-Initio Potential Functions from Energy Partitioned Ab-Initio MODPOT/VRDDO SCF Calculations," NATO Advanced Study Institute on Chemical Reaction Dynamics, Crete, Greece, August 1985.

b. Universities and Other Research Institutions

- * "Ab-Initio Calculations on Large Molecules," University of Tennessee, Knoxville, Tennessee, April 1985.
- * "Ab-Initio Multireference Determinant Configuration Interaction Calculations on Energetic Compounds," Naval Research Laboratories, Washington, D.C., May 1985.

c. At Department of Defense Meetings

- * "Ab-Initio Quantum Methods For and Calculations on Energetic Compounds," ONR/NRL Workshop on Energetic Materials, Initiation Fundamentals, Annapolis, Maryland, October 1984.
- * "Ab-Initio Calculations on Energetic Compounds," ONR Workshop on High Density Explosives, Office of Naval Research, Arlington, Virginia, May 1985.

2. To Be Presented

(* denotes invited lecture)

- * "Ab-Initio MRD-CI Calculations on the $>\text{C} - \text{NO}_2$ Decomposition Pathway of Nitrobenzene," Sanibel Symposium on Quantum Chemistry and Solid State Physics, Marineland, Florida, March 1986.
- * "Ab-Initio Localized Orbital MRD-CI Calculations on the Mechanism of Cationic Polymerization of Oxetane by Protonated Oxetane," Sanibel Symposium on Quantum Chemistry and Solid State Physics, Marineland, Florida, March 1986.
- * "Ab-Initio MRD-CI Calculations on the $>\text{C} - \text{NO}_2$ Decomposition Pathway of Nitrobenzene," Canadian Institute of Chemists Symposium on Computational and Mathematical Chemistry, Saskatoon, Saskatchewan, Canada, June 1986.
- * "Ab-Initio Potentials for Crystals and Ab-Initio Crystal Orbitals," A symposium on Molecules in Physics, Chemistry and Biology, an International Symposium in honor of Professor R. Daudel, Paris, France, June 1986.

C. Papers Published on This ONR Research, October 1984 - September 1985

1. Already Published

- a. "Ab-Initio MODPOT/VRDDO/MERGE Calculations on Energetic Compounds. IV. Nitrocubanes: Mononitro- to Octanitro- Quantum Chemical Calculations and Electrostatic Molecular Potential Contour Maps," P. C. Hariharan, Joyce J. Kaufman, A. H. Lowrey and R. S. Miller. *Int. J. Quantum Chem.* 28, 39-59 (1985).
- b. "Nonempirical Atom-Atom Potentials and Their Applications," W. A. Sokalski, S. Roszak, P. C. Hariharan and Joyce J. Kaufman, *Materials Science*, 10, 487-490 (1984).
- c. "Multireference Determinant CI Calculations and CASSCF Calculations on the $\text{CH}_3 - \text{NO}_2$ Decomposition Pathway of

Nitromethane," Joyce J. Kaufman, P. C. Hariharan, C. Chabalowski and M. Hotokka. An invited paper presented at the Sanibel International Symposium on Quantum Chemistry, Solid-State Theory, Many-Body Phenomena and Computational Quantum Chemistry, Marineland, Florida, March 1985. *Int. J. Quantum Chem. QCS19*, 221-235 (1986).

2. Accepted for Publication and in press

- a. "POLY-CRYST - A Program for Ab-Initio Crystal Orbitals and Polymer Orbitals," J. J. Blaisdell, W. A. Sokalski, P. C. Hariharan and Joyce J. Kaufman. Presented at the International Conference on the Theory of the Structures of Non-Crystalline Solids, Bloomfield Hills, Michigan, June 1985. In press, *J. Non-Crystalline Solids*.
- b. "Ab-Initio CASSCF and Multireference Determinant CI (Configuration Interaction) Calculations on Energetic Compounds," Joyce J. Kaufman, P. C. Hariharan, Matti Hotokka, Cary Chabalowski, Marc van Hemert and S. Roszak. An invited lecture presented at the NATO Advanced Study Institute on Advances in Chemical Reaction Dynamics, Crete, Greece, August 1985. In press in the Proceedings of the Meeting.
- c. "Prediction of Crystal Structures of Energetic Compounds Using Ab-Initio Potential Functions From Energy Partitioned Ab-Initio MODPOT/VRDDO SCF Calculations," Joyce J. Kaufman, P. C. Hariharan, W. A. Sokalski and S. Roszak. An invited lecture presented at the NATO Advanced Study Institute on Advances in Chemical Reaction Dynamics, Crete, Greece, August 1985. In press in the Proceedings of the Meeting.
- d. "Nonempirical Atom-Atom Potentials For Main Components of Intermolecular Interaction Energy," W. A. Sokalski, A. H. Lowrey, S. Roszak, V. Lewchenko, J. Blaisdell, P. C. Hariharan and Joyce J. Kaufman. In press, *Theor. Chim. Acta*.

VII. Project Personnel

The following scientific personnel worked full or part time with this present ONR project.

Joyce J. Kaufman, Ph.D.

Principal Investigator

P. C. Hariharan, Ph.D.

Research Scientist

Overall responsibility for implementing new program developments and conversion to supercomputers.

Quantum chemical calculations on energetic compounds and energetic polymers, three dimensional isopotential electrostatic molecular potential contour EMPC maps, MRD-CI, CASSCF and POLY-CRYST calculations.

Marc van Hemert, Ph.D., Visiting Collaborator[#] (February - March 1985; July 1985).

Conversion of MRD-CI program to CRAY 1M (CTSS) and adapting it to CRAY XMP-12 (COS) and meshing in MOLASYS.

Initiation of MRD-CI calculations on the $>C - NO_2$ decomposition pathway of nitrobenzene.

([#] Permanent address: Gorleaus Laboratories, Leiden, The Netherlands.)

Victor M. Saunders, Ph.D., Visiting Collaborator[∇] (March 1985)

Adapting MRD-CI program to CRAY XMP-12 (COS) and meshing in MOLASYS.

Adapting Daresbury programs to CRAY XMP-12. Analysis of computer requirements for ab-initio crystal orbital calculations on crystals of large explosive molecules.

([∇] Permanent address: Daresbury Laboratories, Daresbury, England)

Szczepan Roszak, Ph.D., Visiting Associate Research Scientist (July 1985 - January 1986)

MRD-CI calculations on the $>C - NO_2$ decomposition pathway of nitrobenzene.

MRD-CI and CASSCF calculations for cationic polymerization - opening the oxetane ring (neutral and protonated)

Matti Hotokka, Ph.D., Visiting Associate Research Scientist* (June - August 1985)

Conversion of the CASSCF program to the CRAY XMP-12 (COS) and meshing in MOLASYS and localization procedure.

Further CASSCF calculations on the $>\text{C} - \text{NO}_2$ decomposition pathway of nitromethane.

Investigation of localized orbital CASSCF calculations on nitromethane and FNOX.

Initial of CASSCF calculation for cationic polymerization opening the oxetane ring.

(* Permanent address: Institutionen For Fysikalisk Kemi, Department of Physical Chemistry, ABO AKEDEMI Porthansgatan, Finland.)

W. A. Sokalski, Ph.D., Visiting Associate Research Scientist (July 1985-September 1985)

Further program development and implementation of energy partitioned components of intermolecular interactions. Conversion to the CRAY 1S (COS) and calculations.

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